

PATENT ABSTRACTS OF JAPAN

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(54) PASTE TYPE NICKEL POSITIVE ELECTRODE FOR ALKALINE STORAGE BATTERY

(57)Abstract:

PURPOSE: To provide a positive electrode with less environmental pollution and high charging efficiency at high temperature by specifying the amount of calcium hydroxide with which the surface of nickel hydroxide particle is coated to the weight of nickel hydroxide powder.

CONSTITUTION: The surface of nickel hydroxide powder is coated with 0.05-2.5wt.% calcium hydroxide based on the weight of the nickel hydroxide powder. The nickel hydroxide coated with calcium hydroxide, serving as an active material, is mixed with metallic cobalt and cobalt oxide, and the mixture is filled in a three-dimensional foamed metal substrate to form a positive electrode. Cadmium by which influence on environmental pollution is feared is not used, an oxide or a hydroxide of calcium by which increase in capacity is suppressed is not mixed with nickel hydroxide, the life of a battery is increased, and drop in charging efficiency at high temperature is suppressed.

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CLAIMS

[Claim(s)]

[Claim 1] The paste type nickel positive electrode for alkaline batteries with which the nickel hydroxide powder which coated the particle front face with the calcium hydroxide is used as the principal component of an active material, and the amount of the calcium hydroxide with which is what filled up the three-dimensions foam metal base with mixture with this active material, metal cobalt, and cobalt oxide, and a particle front face is coated is characterized by being 0.05% to 2.5% to nickel hydroxide powder weight.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About the paste type nickel positive electrode for alkaline batteries, in more detail, this invention uses as an electrode base the Motoki Mitsugi object which makes a foam metal representation, for example, relates to the nickel positive electrode of a nickel-hydrogen battery.

[0002]

[Description of the Prior Art] Conventionally, approaches, such as an electrolytic decomposition process and the chemistry sinking-in method, were used for the porous nickel sintering plate, and what was filled up with the nickel hydroxide used as an active material was used for the nickel positive electrode used for the alkaline battery. Moreover, recently, the nickel felt base which consists of a sponge-like metal nickel porous body which is a Motoki Mitsugi object, or nickel fiber is used as an electrode base, and the nickel positive electrode of the high capacity filled up with the paste-like mixture which contains in this the nickel hydroxide powder which is an active material is also proposed. In order to fill up a direct porous body with the nickel hydroxide which a process is not only simplified, but is an active material as compared with the conventional sintering type nickel positive electrode, the pack density of an active material goes up, and manufacture of the nickel positive electrode of high capacity is possible for the approach using a sponge-like metal nickel porous body. However, since this approach is inferior to a sintering type nickel positive electrode at current collection nature, the oxide of a lot of metal cobalt and cobalt, a hydroxide, etc. are added, it must improve and charge-and-discharge effectiveness and an active material utilization factor cannot necessarily be referred to as becoming large high capacity-ization.

[0003]

[Problem(s) to be Solved by the Invention] The charge and discharge of the nickel hydroxide which is an active material are usually carried out by the paste type nickel positive electrode between beta mold oxy-nickel hydroxide and beta mold nickel hydroxide like a sintering type nickel positive electrode. however -- the case where overcharge by the high current etc. is performed -- ** from beta mold oxy-nickel hydroxide -- it changes to the compound called high gamma mold oxy-nickel hydroxide. In order for a nickel positive-electrode plate to expand and to incorporate the potassium ion in water or the electrolytic solution during a crystal further although discharge capacity increases if this gamma mold oxy-nickel hydroxide generates, liquid absorption of the electrolytic solution beyond the need will be carried out. Generally, by the closed mold cell, since the electrolytic solution is regulated from worries about a liquid spill, if liquid absorption of the electrolytic solution is carried out to a nickel positive electrode in this way beyond the need, the electrolytic solution in a separator will decrease, the so-called electrolytic-solution **** will be produced, and the problem that the internal resistance of a cell increases and the charge-and-discharge cycle life of a cell becomes short will arise. Moreover, when it charges according to the low charging rate of 0.1CmA extent in an ambient atmosphere (40 degrees C and 50 degrees C),

charging efficiency falls and the problem that a predetermined discharge capacity is not obtained arises.

[0004] What carried out mixed crystal of cadmium, the zinc, etc. into 1 nickel hydroxide is used as an active material to such a problem until now. 2) Let what mixed oxides and hydroxides, such as cadmium, and zinc, calcium, with nickel hydroxide be an electrode. There was such an approach. As for cadmium, by carrying out mixed crystal into nickel hydroxide, it is possible by being able to control generation of gamma mold oxy-nickel hydroxide, and adding a cadmium oxide and a hydroxide in a nickel positive electrode to make the charging efficiency at the time of an elevated temperature increase. However, cadmium may cause environmental pollution and there is no change in cadmium being carried into the interior of a cell very much about which approach of the approach of carrying out mixed crystal to nickel hydroxide, and the approach of carrying out adding after mixing of an oxide or the hydroxide. By the nickel-hydrogen battery developed especially recently, since the hydrogen storing metal alloy with little environmental pollution is used for the negative electrode unlike the nickel cadmium battery, if cadmium is not used for a nickel positive-electrode plate, an entire cadmium free battery is made. Since it is such, as for addition of cadmium, withholding will be desirable from now on. Zinc can make the charging efficiency at the time of an elevated temperature increase by carrying out mixed crystal into nickel hydroxide like cadmium by being able to control generation of gamma mold oxy-nickel hydroxide, and adding a zincky oxide and a zincky hydroxide to a nickel positive electrode. Moreover, since there is little effect on environmental pollution like cadmium, it is put in practical use partly. However, the zinc of control of gamma mold oxy-nickel hydroxide or the increment in the charging efficiency at the time of an elevated temperature is small as compared with cadmium, and is not a thing until it satisfies the engine performance demanded.

[0005] From such a background, it is supposed by adding oxides and hydroxides, such as calcium, to a nickel positive electrode by JP,5-101825,A that it is possible for it to be compatible in control of gamma mold oxy-nickel hydroxide and the increment in the charging efficiency at the time of an elevated temperature. However, by this approach, calcium has the remarkable problem that effectiveness is not seen, if amount addition is not carried out. A calcium oxide and a hydroxide can be twisted ** quantity, it is difficult for pack density not to go up but to high-capacity-ize, when pasting and filling up a Motoki Mitsugi object since solubility is small, and it will spoil the advantage of a paste type nickel positive electrode. In a paste type nickel positive electrode, using calcium with little effect on environmental pollution, this invention is high capacity, and controls generation of gamma mold oxy-nickel hydroxide, and offers the nickel positive electrode which the charging efficiency at the time of an elevated temperature also increased sharply.

[0006]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention uses as a principal component the nickel hydroxide powder which coated the particle front face with the calcium hydroxide, it is what filled up the three-dimensions foam metal base with mixture with this active material, metal cobalt, and cobalt oxide, and the amount of the calcium hydroxide with which a particle front face is coated makes it 0.05 to 2.5% to nickel hydroxide powder weight.

[0007]

[Function] Without it seeming that the oxide and hydroxide of calcium which do not use the cadmium with which we are anxious about the effect on environmental pollution, and spoil high capacity-ization which is the advantage of a paste type nickel positive electrode are mix with nickel hydroxide according to the means of this invention, gamma mold oxy-nickel hydroxide can be control effectively at the time of overcharge, the liquid absorption of the electrolytic solution can be suppress, and the reinforcement of a cell can be attain. Moreover, decline in the charging efficiency in the low charging rate at the time of an elevated temperature can also be suppressed.

[0008]

[Example] Use to a nickel-hydrogen battery is made into an example, and the paste type nickel positive electrode by this invention is explained to a detail below. The nickel hydroxide used for the usual active material was produced by the following approaches. the nickel-sulfate water solution prepared so that the amount of nickel might become 5wt(s)% -- 30wt(s)% -- it agitated violently, being dropped with the speed of 2 ml/min. into a sodium-hydroxide water solution. Temperature of the sodium-hydroxide water solution at this time is made into 30 degrees C, a bath is heated to 50 degrees C after dropping termination, and after carrying out heating maintenance for 3 hours, the nickel hydroxide particle whose particle diameter is about 15 micrometers was deposited. Then, the nickel hydroxide powder used as an active material was obtained by rinsing and drying. Next, by the approach almost same with producing the above-mentioned nickel hydroxide, the nickel hydroxide powder which coated the nickel hydroxide front face with the 0.03wt(s)% to 3.0wt(s)% calcium hydroxide was obtained by using a liquid presentation as a calcium sulfate.

[0009] [Battery A] (example by this invention)

It mixed with the hydroxypropyl-methylcellulose water solution and distilled water which prepared the nickel hydroxide powder which coated the front face with the 0.05wt(s)% calcium hydroxide by the above-mentioned approach, cobalt oxide powder, and metal cobalt powder to 3wt(s)%, and the paste was produced. The solid content presentation at this time was mixed so that it might become hydroxypropyl-methylcellulose 0.45wt% metal cobalt 1.0wt% cobalt oxide 4.0wt% nickel hydroxide 94.55wt%. The foaming nickel base of 1.2mm in thickness and 94% of porosity was filled up with this paste, and the paste type nickel positive electrode with width of face of 40mm, a die length [of 81mm], and a thickness of 0.6mm was obtained by drying, pressing and judging. The capacity consistencies of the nickel positive electrode at this time were 620 mAh/cm³. Using the hydrogen storing metal alloy of the presentation which consists of Mm-nickel-Co-aluminum-Mn prepared by the conventional approach, the negative electrode ground this hydrogen storing metal alloy using machine crushers, such as a ball mill, and what kneaded as a binder what particle diameter set to about 60 to about 100 micrometers, and filled up the foaming nickel base with the hydroxypropyl methylcellulose for it was used for it. The capacity consistencies of the hydrogen pole at this time were about 1200 mAh/cm³. Using the nonwoven fabric separator made of nylon, these nickel positive electrodes and a hydrogen pole were wound so that the outermost periphery might be on a hydrogen pole side. After inserting this electrode group in a cylindrical shape cell container, it carried out specified quantity pouring in of the 31wt% potassium-hydroxide water solution, and the sealing form nickel-hydrogen battery of AA size was produced. The geometric capacity of this cell is 1200mAh(s).

[0010] [Battery B] (example by this invention)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 0.08wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0011] [Battery C] (example by this invention)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 0.1wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0012] [Battery D] (example by this invention)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 0.5wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0013] [Battery E] (example by this invention)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 1.0wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0014] [Battery F] (example by this invention)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 1.5wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0015] [Battery G] (example by this invention)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 2.0wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0016] [Battery H] (example by this invention)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 2.5wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0017] [Battery I] (example 1 of a comparison)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which has not coated a front face with the calcium hydroxide produced by the above mentioned approach. The geometric capacity of this cell is 1200mAh(s).

[0018] [Battery J] (example 2 of a comparison)

The paste which mixed calcium-hydroxide powder 1% further in addition to cobalt oxide powder and metal cobalt powder was produced using the nickel hydroxide powder which has not coated a front face with the calcium hydroxide produced by the above mentioned approach. The solid content presentation at this time was mixed so that it might become hydroxypropyl-methylcellulose 0.45wt% calcium-hydroxide 1.0wt% metal cobalt 1.0wt% cobalt oxide 4.0wt% nickel hydroxide 93.55wt%. The foaming nickel base of 1.2mm in thickness and 94% of porosity was filled up with this paste, and the paste type nickel positive electrode with width of face of 40mm, a die length [of 81mm], and a thickness of 0.6mm was obtained by drying, pressing and judging. The capacity consistencies of the nickel positive electrode at this time were 620 mAh/cm³ equivalent to the nickel positive electrode by this invention. Other cell configurations produced the nickel-hydrogen battery made to be the same as that of Battery A using this positive electrode. The geometric capacity of this cell is 1200mAh(s).

[0019] [Battery K] (example 3 of a comparison)

The paste which mixed calcium-hydroxide powder 5% further in addition to cobalt oxide powder and metal cobalt powder was produced using the nickel hydroxide powder which has not coated a front face with the calcium hydroxide produced by the above mentioned approach. The solid content presentation at this time was mixed so that it might become hydroxypropyl-methylcellulose 0.45wt% calcium-hydroxide 5.0wt% metal cobalt 1.0wt% cobalt oxide 4.0wt% nickel hydroxide 89.55wt%. The foaming nickel base of 1.2mm in thickness and 94% of porosity was filled up with this paste, and the paste type nickel positive electrode with width of face of 40mm, a die length [of 81mm], and a thickness of 0.6mm was obtained by drying, pressing and judging. The paste which added calcium-hydroxide powder to 5.0wt(s)% had the low filling factor to a Motoki Mitsugi object, and the capacity consistencies of the nickel positive electrode at this time were 570 mAh/cm³. Other cell configurations produced the nickel-hydrogen battery made to be the same as that of Battery A using this positive electrode. The geometric capacity of this cell is 1100mAh(s).

[0020] [Battery L] (example 4 of a comparison)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 0.03wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0021] [Battery M] (example 5 of a comparison)

Battery A and the nickel-hydrogen battery of the same configuration were produced using the nickel hydroxide powder which coated the front face of nickel hydroxide powder with the 3.0wt(s)% calcium hydroxide. The geometric capacity of this cell is 1200mAh(s).

[0022] As evaluation of the cell using these paste type nickel positive electrodes, cycle life test and

a temperature characteristic trial were performed. Cycle life test carried out the perfect charge and discharge to which charge is discharged by 1CmA and it discharges discharge to termination electrical-potential-difference 1.0V by 1CmA for 90 minutes. Moreover, the temperature characteristic was carried out at charge-and-discharge same temperature in 20 degrees C of ambient temperature, 40 degrees C, and 50 degrees C according to the conditions on which charge is discharged by 0.1CmA(s) and it discharges discharge to termination electrical-potential-difference 1.0V by 0.2CmA(s) for 900 minutes.

[0023] The cycle-life property of the cell (batteries A, B, C, D, E, F, G, and H) using a paste type nickel positive electrode and the cell (batteries I, J, K, L, and M) of the examples 1-5 of a comparison by this invention was shown in drawing 1. The cell (example 1 of a comparison) using what does not add the calcium-hydroxide powder which is the conventional paste type nickel positive electrode, and has not coated a nickel hydroxide front face with a calcium hydroxide became a life by the increment in the internal resistance by ***** near 300 cycles. moreover, calcium-hydroxide powder -- 1.0wt(s)% -- the cell (example 2 of a comparison) using the added paste type nickel positive electrode also became a life by the increment in the internal resistance by ***** near [as the cell of the example 1 of a comparison / almost same] 325 cycles. calcium-hydroxide powder -- 5.0wt(s)% -- although the life cycle maintained the cell (example 3 of a comparison) using the added paste type nickel positive electrode to near 500 cycles, it was made net volume from the lowness of pack density, and the lowness of an active material utilization factor, and only the capacity of 1000mAh extent was obtained. Moreover, even if it was a cell using the paste type nickel positive electrode which consists of nickel hydroxide powder which coated the front face with the calcium hydroxide, the cell (example 4 of a comparison) using what has the amount of coatings fewer than 0.05% on the front face of nickel hydroxide, and the cell (example 5 of a comparison) using what was coated were properties which are inferior to the cell of the former [**** / that the addition effectiveness of a calcium hydroxide is not seen] from both decline in an active material utilization factor etc. On the other hand, each cell (batteries A, B, C, D, E, F, G, and H) using the paste type nickel positive electrode by this invention showed the life property of 500 or more cycles, with high capacity maintained.

[0024] The temperature characteristic test result of the cell (batteries I, J, K, L, and M) of the examples 1-5 of a comparison was shown in Table 1 in the cell (batteries A, B, C, D, E, F, G, and H) using the paste type nickel positive electrode by this invention, and Table 2, respectively. 40 degrees C / 20-degree-C capacity factor was [50 degrees C / 20-degree-C capacity factor of the cell (example 1 of a comparison) using what does not add the calcium-hydroxide powder which is the conventional paste type nickel positive electrode, and has not coated a nickel hydroxide front face with a calcium hydroxide] 50% 75%. moreover, calcium-hydroxide powder -- 1.0wt(s)% -- although, as for 40 degrees C / 20-degree-C capacity factor, effectiveness was seen 80% and a little, as for the cell (example 2 of a comparison) using the added paste type nickel positive electrode, effectiveness was hardly put at 52%, as for 50 degrees C / 20-degree-C capacity factor. calcium-hydroxide powder -- 5.0wt(s)% -- as for the cell (example 3 of a comparison) using the added paste type nickel positive electrode, also in 50 degrees C, effectiveness was somewhat put [40 degrees C / 20-degree-C capacity factor] for 50 degrees C / 20-degree-C capacity factor at 70% 88%. Even if it was a cell using the paste type nickel positive electrode which consists of nickel-hydroxide powder which coated the front face with the calcium hydroxide, the addition effectiveness of a calcium hydroxide was not seen and, as for the cell (example 4 of a comparison) using what has the amount of coatings fewer than 0.05% on the front face of nickel hydroxide, or the cell (example 5 of a comparison) using what was coated, a difference was hardly regarded as the cell (example 1 of a comparison) using the conventional paste type nickel pole. On the other hand, as for the cell (batteries A, B, C, D, E, F, G, and H) using the paste type nickel positive electrode by this invention, 40 degrees C / 20-degree-C capacity factor all excelled [capacity factor / 50 degrees C / 20 degree-C] the conventional thing in the property with 78% or more 90% or more.

[0025]

[Table 1]

	40℃/20℃	50℃/20℃
蓄電池A (本發明)	90%	78%
蓄電池B (本發明)	90%	78%
蓄電池C (本發明)	92%	80%
蓄電池D (本發明)	95%	85%
蓄電池E (本發明)	95%	88%
蓄電池F (本發明)	95%	88%
蓄電池G (本發明)	95%	89%
蓄電池H (本發明)	93%	85%

[0026]

[Table 2]

	40℃/20℃	50℃/20℃
蓄電池I (比較例1)	75%	50%
蓄電池J (比較例2)	80%	52%
蓄電池K (比較例3)	88%	70%
蓄電池L (比較例4)	78%	50%
蓄電池M (比較例5)	82%	58%

[0027]

[Effect of the Invention] As mentioned above, without it seeming that the oxide and hydroxide of calcium which do not use the cadmium with which we be anxious about the effect on environmental pollution, and spoil high capacity-ization which be the advantage of a paste type nickel positive electrode be mix with nickel hydroxide according to the means of this invention, gamma mold oxy-nickel hydroxide can be control effectively at the time of overcharge, the liquid absorption of the electrolytic solution can be suppress, and the reinforcement of a cell can be attain. Moreover, decline in the charging efficiency in the low charging rate at the time of an elevated temperature can also be suppressed.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the cycle-life property of the cell (batteries A, B, C, D, E, F, G, and H) using a paste type nickel positive electrode, and the cell of the examples 1-5 (batteries I, J, K, L, and M) of a comparison by this invention.

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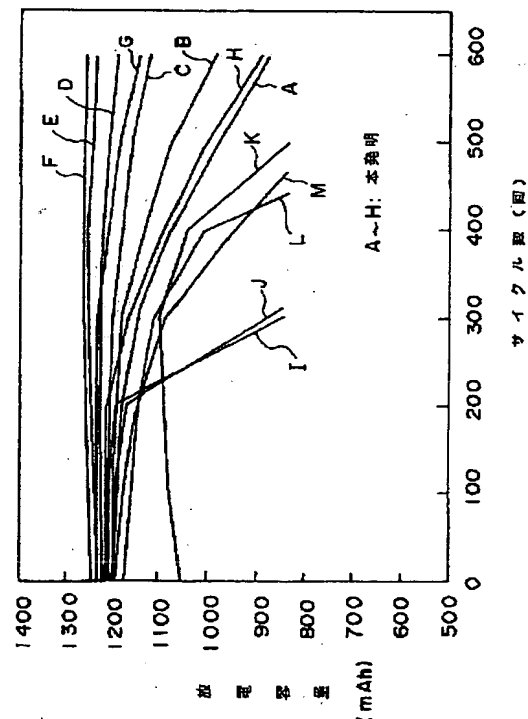
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(54) 【発明の名称】 アルカリ蓄電池用ペースト式ニッケル正極

(57) 【要約】

【目的】 ペースト式ニッケル正極の利点である高容量化を損なうことなく、電池における寿命特性、高温下の充電特性に優れたアルカリ蓄電池用ペースト式ニッケル正極を得る。

【構成】 水酸化カルシウムを粒子表面にコーティングした水酸化ニッケル粉末を活物質の主成分とし、該活物質と金属コバルトおよびコバルト酸化物との混合物を三次元発泡金属基体に充填したアルカリ蓄電池用ペースト式ニッケル正極。



【特許請求の範囲】

【請求項1】水酸化カルシウムを粒子表面にコーティングした水酸化ニッケル粉末を活物質の主成分とし、該活物質と金属コバルトおよびコバルト酸化物との混合物を三次元発泡金属基体に充填したもので、粒子表面にコーティングする水酸化カルシウムの量が水酸化ニッケル粉末重量に対して0.05%から2.5%であることを特徴とするアルカリ蓄電池用ペースト式ニッケル正極。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、アルカリ蓄電池用ペースト式ニッケル正極に関するもので、さらに詳しくは、発泡金属を代表とする三次元基体を電極基体とする、例えばニッケル-水素蓄電池のニッケル正極に関するものである。

【0002】

【従来の技術】従来、アルカリ蓄電池に用いられているニッケル正極には、多孔性のニッケル焼結板に、電解法や化学含浸法などの方法を用いて、活物質となる水酸化ニッケルを充填したものが用いられていた。また、最近では三次元基体であるスポンジ状金属ニッケル多孔体やニッケル繊維からなるニッケルフェルト基体などを電極基体とし、これに活物質である水酸化ニッケル粉末を含むペースト状混合物を充填した高容量のニッケル正極も提案されている。スポンジ状金属ニッケル多孔体を用いる方法は、従来の焼結式ニッケル正極と比較して工程が簡略化されるだけでなく、活物質である水酸化ニッケルを直接多孔体に充填するため活物質の充填密度が上がり、高容量のニッケル正極の製造が可能である。しかし、この方法は焼結式ニッケル正極よりも集電性に劣るため、大量の金属コバルトやコバルトの酸化物、水酸化物等を添加し、充放電効率および活物質利用率を向上しなければならず、必ずしも大幅な高容量化になるとは言えない。

【0003】

【発明が解決しようとする課題】ペースト式ニッケル正極は焼結式ニッケル正極と同様に、通常、活物質である水酸化ニッケルが β 型オキシ水酸化ニッケルと β 型水酸化ニッケルの間で充放電される。しかし、大電流による過充電などを行った場合には β 型オキシ水酸化ニッケルから嵩高い γ 型オキシ水酸化ニッケルと呼ばれる化合物に変化する。この γ 型オキシ水酸化ニッケルが生成すると、放電容量は増加するがニッケル正極板は膨張し、さらに結晶中に水や電解液中のカリウムイオンを取り込んでしまうため、必要以上の電解液を吸液してしまう。一般的に密閉型電池では、漏液の心配から電解液が規制されているため、このようにニッケル正極に電解液を必要以上に吸液されると、セパレータ中の電解液が少なくなり、いわゆる電解液涸れを生じ、電池の内部抵抗が増加して電池の充放電サイクル寿命が短くなるという問題が

起こる。また、40℃や50℃の雰囲気中で0.1CmA程度の低充電率で充電された場合、充電効率が低下し所定の放電容量が得られないという問題が起こる。

【0004】このような問題に対し、今まで、1)水酸化ニッケル中にカドミウムや亜鉛などを混晶したものを活物質として用いる。2)カドミウムや亜鉛、カルシウムなどの酸化物や水酸化物を水酸化ニッケルとともに混合したものを電極とする。このような方法があった。カドミウムは水酸化ニッケル中に混晶することにより、 γ 型オキシ水酸化ニッケルの生成を抑制することができ、またカドミウム酸化物や水酸化物をニッケル正極中に添加することにより、高温時の充電効率を増加させることが可能である。しかしながら、カドミウムは環境汚染の原因となる可能性があり、水酸化ニッケルに混晶する方法、酸化物や水酸化物を後添加する方法のいずれの方法をとっても、電池内部にカドミウムが持ち込まれることに変わりはない。特に最近開発されたニッケル-水素蓄電池では、ニッケル-カドミウム蓄電池と異なり負極には環境汚染の少ない水素吸蔵合金が用いられているため、ニッケル正極板にカドミウムを使用しなければ、まったくのカドミウムフリー蓄電池ができる。このことから今後、カドミウムの添加は差し控えていくことが望ましい。亜鉛はカドミウムと同様に水酸化ニッケル中に混晶することにより、 γ 型オキシ水酸化ニッケルの生成を抑制することができ、また亜鉛の酸化物や水酸化物をニッケル正極に添加することにより高温時の充電効率を増加させることができる。その上、カドミウムのように環境汚染への影響が少ないことから一部で実用化されている。しかし、亜鉛はカドミウムと比較すると γ 型オキシ水酸化ニッケルの抑制や高温時の充電効率の増加は小さく、要求されている性能を満足させるまでのものではない。

【0005】このような背景から、特開平5-101825号公報では、カルシウムなどの酸化物や水酸化物をニッケル正極に添加することにより、 γ 型オキシ水酸化ニッケルの抑制と高温時の充電効率の増加を両立することが可能とされている。しかし、この方法ではカルシウムはかなりの量添加しなければ効果が見られないという問題がある。カルシウム酸化物、水酸化物は嵩高なうえ溶解度が小さいため、ペースト化して三次元基体に充填する場合、充填密度が上がらず、高容量化することが困難であり、ペースト式ニッケル正極の利点を損なってしまう。本発明は、ペースト式ニッケル正極において、環境汚染への影響が少ないカルシウムを用い、高容量でかつ γ 型オキシ水酸化ニッケルの生成を抑制し、高温時の充電効率も大幅に増加したニッケル正極を提供するものである。

【0006】

【課題を解決するための手段】上記課題を解決するために、本発明は、水酸化カルシウムを粒子表面にコーティ

ングした水酸化ニッケル粉末を主成分とし、該活物質と金属コバルトおよびコバルト酸化物との混合物を三次元発泡金属基体に充填したもので、粒子表面にコーティングする水酸化カルシウムの量が水酸化ニッケル粉末重量に対して0.05%から2.5%としたものである。

【0007】

【作用】本発明の手段によると、環境汚染への影響が懸念されるカドミウムを使用せず、また、ペースト式ニッケル正極の利点である高容量化を損なうカルシウムの酸化物や水酸化物を水酸化ニッケルとともに混合することなく、過充電時に効果的に γ -型オキシ水酸化ニッケルを抑制し、電解液の吸液を抑え電池の長寿命化を達成することができる。また、高温時の低充電率での充電効率の低下も抑えることができる。

【0008】

【実施例】本発明によるペースト式ニッケル正極を、ニッケル-水素蓄電池への使用を例にして以下詳細に説明する。通常の活物質に用いる水酸化ニッケルは以下の方法により作製した。ニッケル量が5 wt %になるように調製した硫酸ニッケル水溶液を30 wt %水酸化ナトリウム水溶液中に2 ml/min.の速さで滴下しながら激しく攪拌した。この時の水酸化ナトリウム水溶液の温度は30℃とし、滴下終了後、浴を50℃まで加熱し、3時間加熱保持したのち、粒子径が約15 μ m程度の水酸化ニッケル粒子を析出させた。その後、水洗、乾燥することにより活物質とする水酸化ニッケル粉末を得た。次に上記水酸化ニッケルを作製するのとほぼ同様の方法で、液組成を硫酸カルシウムとすることにより、水酸化ニッケル表面に0.03 wt %から3.0 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を得た。

【0009】[蓄電池A] (本発明による実施例)

上記の方法により表面に0.05 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末と酸化コバルト粉末、金属コバルト粉末を3 wt %に調製したヒドロキシプロピルメチルセルロース水溶液および蒸留水とともに混合し、ペーストを作製した。この時の固形分組成は、水酸化ニッケル94.55 wt %、酸化コバルト4.0 wt %、金属コバルト1.0 wt %、ヒドロキシプロピルメチルセルロース0.45 wt %となるように混合した。このペーストを厚さ1.2 mm、多孔度94%の発泡ニッケル基体に充填し、乾燥、プレス、裁断することにより、幅40 mm、長さ81 mm、厚さ0.6 mmのペースト式ニッケル正極を得た。この時のニッケル正極の容量密度は620 mAh/cm³であった。負極は、従来の方法により調製したMm-Ni-Co-Al-Mnからなる組成の水素吸蔵合金を用い、この水素吸蔵合金をボールミルなどの機械粉砕器を用いて粉砕し、粒子径が約60 μ mから100 μ m程度としたものを、ヒドロキシプロピルメチルセルロースをバインダと

して混練し、発泡ニッケル基体に充填したものをを用いた。この時の水素極の容量密度は約1200 mAh/cm³であった。これらのニッケル正極、水素極をナイロン製の不織布セパレータを用いて、最外周が水素極側になるように捲回した。この電極群を円筒形電池容器に挿入後、31 wt %水酸化カリウム水溶液を所定量注液しAAサイズの密閉形ニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0010】[蓄電池B] (本発明による実施例)

水酸化ニッケル粉末の表面に0.08 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0011】[蓄電池C] (本発明による実施例)

水酸化ニッケル粉末の表面に0.1 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0012】[蓄電池D] (本発明による実施例)

水酸化ニッケル粉末の表面に0.5 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0013】[蓄電池E] (本発明による実施例)

水酸化ニッケル粉末の表面に1.0 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0014】[蓄電池F] (本発明による実施例)

水酸化ニッケル粉末の表面に1.5 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0015】[蓄電池G] (本発明による実施例)

水酸化ニッケル粉末の表面に2.0 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0016】[蓄電池H] (本発明による実施例)

水酸化ニッケル粉末の表面に2.5 wt %の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0017】[蓄電池I] (比較例1)

前記した方法により作製した水酸化カルシウムを表面にコーティングしていない水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200 mAhである。

【0018】[蓄電池J] (比較例2)

前記した方法により作製した水酸化カルシウムを表面に

コーティングしていない水酸化ニッケル粉末を用い、酸化コバルト粉末、金属コバルト粉末に加えさらに水酸化カルシウム粉末を1%混合したペーストを作製した。この時の固形分組成は、水酸化ニッケル93.55wt%、酸化コバルト4.0wt%、金属コバルト1.0wt%、水酸化カルシウム1.0wt%、ヒドロキシプロピルメチルセルロース0.45wt%となるように混合した。このペーストを厚さ1.2mm、多孔度94%の発泡ニッケル基体に充填し、乾燥、プレス、裁断することにより、幅40mm、長さ81mm、厚さ0.6mmのペースト式ニッケル正極を得た。この時のニッケル正極の容量密度は本発明によるニッケル正極と同等の62.0mAh/cm²であった。この正極を用い、その他の電池構成は蓄電池Aと同様にしたニッケル-水素蓄電池を作製した。この電池の理論容量は1200mAhである。

【0019】[蓄電池K] (比較例3)

前記した方法により作製した水酸化カルシウムを表面にコーティングしていない水酸化ニッケル粉末を用い、酸化コバルト粉末、金属コバルト粉末に加えさらに水酸化カルシウム粉末を5%混合したペーストを作製した。この時の固形分組成は、水酸化ニッケル89.55wt%、酸化コバルト4.0wt%、金属コバルト1.0wt%、水酸化カルシウム5.0wt%、ヒドロキシプロピルメチルセルロース0.45wt%となるように混合した。このペーストを厚さ1.2mm、多孔度94%の発泡ニッケル基体に充填し、乾燥、プレス、裁断することにより、幅40mm、長さ81mm、厚さ0.6mmのペースト式ニッケル正極を得た。水酸化カルシウム粉末を5.0wt%まで添加したペーストは三次元基体への充填率が低く、この時のニッケル正極の容量密度は57.0mAh/cm²であった。この正極を用い、その他の電池構成は蓄電池Aと同様にしたニッケル-水素蓄電池を作製した。この電池の理論容量は1100mAhである。

【0020】[蓄電池L] (比較例4)

水酸化ニッケル粉末の表面に0.03wt%の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200mAhである。

【0021】[蓄電池M] (比較例5)

水酸化ニッケル粉末の表面に3.0wt%の水酸化カルシウムをコーティングした水酸化ニッケル粉末を用い、蓄電池Aと同様の構成のニッケル-水素蓄電池を作製した。この電池の理論容量は1200mAhである。

【0022】これらのペースト式ニッケル正極を用いた電池の評価として、サイクル寿命試験及び温度特性試験を行った。サイクル寿命試験は充電を1CmAで90分、放電を1CmAで終止電圧1.0Vまで放電する完全充放電を実施した。また、温度特性は充電を0.1C

mAで900分、放電を0.2CmAで終止電圧1.0Vまで放電する条件で雰囲気温度20℃、40℃、50℃にて充放電同一温度で実施した。

【0023】図1に本発明によるペースト式ニッケル正極を用いた電池(蓄電池A, B, C, D, E, F, G, H)と比較例1から5の電池(蓄電池I, J, K, L, M)のサイクル寿命特性を示した。従来のペースト式ニッケル正極である水酸化カルシウム粉末を添加せず、また水酸化ニッケル表面に水酸化カルシウムもコーティングしていないものを用いた電池(比較例1)は、300サイクル付近で液漏れによる内部抵抗の増加により寿命となった。また、水酸化カルシウム粉末を1.0wt%添加したペースト式ニッケル正極を用いた電池(比較例2)も、比較例1の電池とほぼ同じの325サイクル付近で、液漏れによる内部抵抗の増加により寿命となった。水酸化カルシウム粉末を5.0wt%添加したペースト式ニッケル正極を用いた電池(比較例3)は、寿命サイクルは500サイクル付近まで維持したが、充填密度の低さと活物質利用率の低さから実容量にして1000mAh程度の容量しか得られなかった。また、水酸化カルシウムを表面にコーティングした水酸化ニッケル粉末からなるペースト式ニッケル正極を用いた電池であっても、水酸化ニッケル表面へのコーティング量が0.05%より少ないものを用いた電池(比較例4)や2.5%よりも多くコーティングしたものを用いた電池(比較例5)は、水酸化カルシウムの添加効果が見られなかったり、活物質利用率の低下などから共に従来の電池より劣る特性であった。これに対し、本発明によるペースト式ニッケル正極を用いた電池(蓄電池A, B, C, D, E, F, G, H)は、どれも高容量を維持したまま500サイクル以上の寿命特性を示した。

【0024】表1に本発明によるペースト式ニッケル正極を用いた電池(蓄電池A, B, C, D, E, F, G, H)、表2に比較例1から5の電池(蓄電池I, J, K, L, M)の温度特性試験結果をそれぞれ示した。従来のペースト式ニッケル正極である水酸化カルシウム粉末を添加せず、また水酸化ニッケル表面に水酸化カルシウムもコーティングしていないものを用いた電池(比較例1)は、40℃/20℃容量比が75%、50℃/20℃容量比が50%であった。また、水酸化カルシウム粉末を1.0wt%添加したペースト式ニッケル正極を用いた電池(比較例2)は、40℃/20℃容量比は80%と若干効果が見られたが、50℃/20℃容量比は52%とほとんど効果が見られなかった。水酸化カルシウム粉末を5.0wt%添加したペースト式ニッケル正極を用いた電池(比較例3)は、40℃/20℃容量比が88%、50℃/20℃容量比が70%と、50℃においても効果が多少見られた。水酸化カルシウムを表面にコーティングした水酸化ニッケル粉末からなるペースト式ニッケル正極を用いた電池であっても、水酸化ニ

ケル表面へのコーティング量が0.05%より少ないものを用いた電池(比較例4)や2.5%よりも多くコーティングしたものを用いた電池(比較例5)は水酸化カルシウムの添加効果が見られず、従来のペースト式ニッケル極を用いた電池(比較例1)とほとんど差が見られなかった。これに対し、本発明によるペースト式ニッケ

ル正極を用いた電池(蓄電池A, B, C, D, E, F, G, H)は、40℃/20℃容量比が90%以上、50℃/20℃容量比が78%以上と、どれも従来のものよりも特性に優れていた。

【0025】

【表1】

	40℃/20℃	50℃/20℃
蓄電池A(本発明)	90%	78%
蓄電池B(本発明)	90%	78%
蓄電池C(本発明)	92%	80%
蓄電池D(本発明)	95%	85%
蓄電池E(本発明)	95%	88%
蓄電池F(本発明)	95%	88%
蓄電池G(本発明)	95%	89%
蓄電池H(本発明)	93%	85%

【0026】

【表2】

	40℃/20℃	50℃/20℃
蓄電池I(比較例1)	75%	50%
蓄電池J(比較例2)	80%	52%
蓄電池K(比較例3)	88%	70%
蓄電池L(比較例4)	78%	50%
蓄電池M(比較例5)	82%	58%

【0027】

【発明の効果】以上のように、本発明の手段によると環境汚染への影響が懸念されるカドミウムを使用せず、また、ペースト式ニッケル正極の利点である高容量化を損なうカルシウムの酸化物や水酸化物を水酸化ニッケルとともに混合するようなこともなく、過充電時に効果的にγ型オキシ水酸化ニッケルを抑制し、電解液の吸液を抑え電池の長寿命化を達成することができる。また、高温

時の低充電率での充電効率の低下も抑えることができる。

【図面の簡単な説明】

【図1】本発明によるペースト式ニッケル正極を用いた電池(蓄電池A, B, C, D, E, F, G, H)と比較例1から5(蓄電池I, J, K, L, M)の電池のサイクル寿命特性を示した図である。

【図1】

